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SPECTROSCOPIES TO MECHANICAL (H) PURDUE UNIV LAFAYETTE IN
DEPT OF CHEMISTRY H J WEAVER ET AL. 25 SEP 87 18-75
AD8014-86-R-0336

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Technical Report No. 75

**Some Applications of Surface Raman and Infrared Spectroscopies
to Mechanistic Electrochemistry Involving Adsorbed Species**

by

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Prepared for Publication

in the

J. Electron. Spect. Related Phen.

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September 25, 1987

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REPORT DOCUMENTATION PAGE

1. REPORT SECURITY CLASSIFICATION Unclassified		16. DISTRIBUTION STATEMENTS	
2. SECURITY CLASSIFICATION AUTHORITY		3. DISTRIBUTION/AVAILABILITY OF REPORT Approved for public release and sale; its distribution is unlimited.	
3. DECLASSIFICATION/DOWNGRADING (if applicable)		5. MONITORING ORGANIZATION REPORT NUMBER(S)	
4. MONITORING ORGANIZATION REPORT NUMBER(S) Technical Report No. 75		7a. NAME OF MONITORING ORGANIZATION Division of Sponsored Programs Purdue Research Foundation	
5a. NAME OF FUNDING ORGANIZATION Purdue University Department of Chemistry		7b. ADDRESS (City, State, and ZIP Code) Purdue University West Lafayette, Indiana 47907	
5b. ADDRESS (City, State, and ZIP Code) Purdue University Department of Chemistry West Lafayette, Indiana 47907		8. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER Contract No. W00014-86-K-01556	
6a. NAME OF FUNDING SPONSORING ORGANIZATION Office of Naval Research		9. SOURCE OF FUNDING NUMBERS	
6b. ADDRESS (City, State, and ZIP Code) 800 N. Quincy Street Arlington, VA 22217		PROGRAM ELEMENT NO. PROJECT NO. TASK NO. WORK UNIT ACCESSION N	

11. TITLE (Include Security Classification)

Some Applications of Surface Raman and Infrared Spectroscopies to Mechanistic Electrochemistry Involved Adsorbed Species

12. PERSONAL AUTHOR(S)

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13a. TYPE OF REPORT

Technical

13b. TIME COVERED

FROM 10/1/86 TO 9/30/87

14. DATE OF REPORT (Year, Month, Day)

September 25, 1987

15. PAGE COUNT

17. SUPPLEMENTARY NOTATION

COSATI CODES		
FIELD	GROUP	SUB-GROUP

18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)
surface-enhanced Raman spectroscopy, infrared reflection-adsorption spectroscopy, time-resolved spectra, optical multichannel analyzer, Fourier transfer, linear sweep voltammetry

19. ABSTRACT (Continue on reverse if necessary and identify by block number)

Some methods are outlined by which surface-enhanced Raman spectroscopy (SERS) and infrared reflection-adsorption spectroscopy (IRRAS) can be applied to gain mechanistic information for multistep electrode processes involving adsorbed species. Emphasis is placed on approaches in which time-resolved spectra can be obtained in conjunction with conventional electrochemical techniques, enabling simultaneous vibrational and electrochemical kinetic (current-potential-time) information to be obtained during the evolution of irreversible electrode processes. Specific applications to irreversible electroorganic reactions are outlined, employing optical multichannel analyzer and Fourier transform instrumentation for SERS and IRRAS, respectively, in conjunction with linear sweep voltammetry.

Keywords:

20. DISTRIBUTION/AVAILABILITY OF ABSTRACT <input checked="" type="checkbox"/> UNCLASSIFIED/UNLIMITED <input type="checkbox"/> SAME AS RPT <input type="checkbox"/> DTIC USERS		21. ABSTRACT SECURITY CLASSIFICATION	
22a. NAME OF RESPONDER/INDIVIDUAL		22b. TELEPHONE (include Area Code) 22c. OFFICE SYMBOL	

SOME APPLICATIONS OF SURFACE RAMAN AND INFRARED SPECTROSCOPIES TO MECHANISTIC ELECTROCHEMISTRY INVOLVING ADSORBED SPECIES

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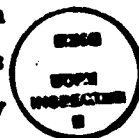
SUMMARY

Some methods are outlined by which surface-enhanced Raman spectroscopy (SERS) and infrared reflection-absorption spectroscopy (IRRAS) can be applied to gain mechanistic information for multistep electrode processes involving adsorbed species. Emphasis is placed on approaches in which time-resolved spectra can be obtained in conjunction with conventional electrochemical techniques, enabling simultaneous vibrational and electrochemical kinetic (current-potential-time) information to be obtained during the evolution of irreversible electrode processes. Specific applications to irreversible electroorganic reactions are outlined, employing optical multichannel analyzer and Fourier transform instrumentation for SERS and IRRAS, respectively, in conjunction with linear sweep voltammetry.

INTRODUCTION

Despite the close fundamental connections between chemical phenomena at metal-gas and metal-electrolyte (i.e. electrochemical) surfaces, decidedly different methods have historically been employed for examining these two important types of interfacial systems. While an increasing variety of molecule-sensitive spectroscopic approaches have been developed with which to examine the former, the attainment of both structural and mechanistic chemical information for the latter has continued to rely chiefly on "conventional electrochemical" (i.e. current-potential-time) approaches. Although a remarkably detailed picture of electrochemical systems can be obtained in this manner, the acquisition of "molecular-level" information as furnished by optical spectroscopies is not only desirable in its own right, but would enable more direct intercomparison with the properties of related metal-gas systems. For

The development of such techniques for in-situ electrochemical purposes has been hampered by the inevitable interferences arising from the necessary presence of bulk-phase solvent and electrolyte. Nevertheless, the development of a number of such techniques is now proceeding apace. Prominent amongst these are surface-enhanced Raman scattering (SERS)¹ and infrared reflection-absorption spectroscopy (IRRAS).² While the latter technique has already found wide application to the characterization of adsorbates at metal-gas interfaces, the former has had relatively little impact in this regard.



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However, both SERS and IRRAS are well suited for electrochemical applications, and indeed can be regarded as providing conveniently complementary techniques for the vibrational characterization of electrochemical adsorbates. A major virtue of the former approach is that the high degree of surface enhancement observed, at least for silver, gold, and copper substrates largely eliminates the solution-phase interferences that plague other surface spectral techniques, enabling the method to be employed in conventional electrochemical cells. The wide spectral range and excellent frequency resolution inherent to Raman spectroscopy also provide major advantages. On the other hand, due to the surface roughening necessary for SERS together with the very nature of the enhancement effect, it is possible that the observed spectra may not reflect the properties of the preponderant adsorbate. Indeed, this perceived difficulty has hindered the acceptance of the technique by electrochemists as well as by other surface scientists.

Although electrochemical IRRAS requires a thin-layer arrangement so to minimize bulk electrolyte interferences and is usable for a more limited range of adsorbates (and frequencies), similar to gas-phase IRRAS it is applicable to a much wider variety of electrode surfaces. An advantage peculiar to the electrochemical variant of IRRAS is that, as an alternative to polarization modulation (PM-IRRAS), removal of bulk-phase interferences can be achieved readily by ratioing spectra obtained at appropriate pairs of electrode potentials.² Such potential-difference infrared (PDIR) methods have the virtue of providing information selectively on potential-dependent phenomena, such as adsorption-desorption and redox processes, that are of particular electrochemical significance.

An important component of our own research activities in electrochemical application of SERS and IRRAS is to employ these techniques to obtain molecular structural information for reactive adsorbates; i.e. those species acting as reactants, intermediates or products in electrode processes. Our applications of SERS for this purpose have been aided substantially by two factors. Firstly, an electrochemical pretreatment procedure is available that yields gold surfaces displaying stable as well as intense SERS.³ The nobility and electrocatalytic properties of gold make this metal a suitable substrate for a wide range of oxidation as well as reduction processes; several such applications of SERS have resulted.^{3,4} Secondly, by depositing thin (a few monolayer) overlayer films on the gold surface, SERS can be imparted both to adsorbates bound to the overlayer⁵ and (in the case of metal oxide layers) to the film itself.^{4,6} This approach therefore provides a means of extending SERS to a range of electrode surfaces beyond the coinage metals themselves.

The aim of this conference paper is to outline some methods by which SERS and IRRAS can yield vibrational structural information of mechanistic

electrochemical significance. We confine discussion here to processes involving adsorbed species; application of IRRAS to reactions involving solution-phase electrogenerated species is a distinct topic which has been dealt with thoroughly elsewhere (e.g. ref. 2b). Emphasis is placed on experiments in which spectra are obtained in conjunction with conventional electrochemical techniques. The application of these approaches to the elucidation of multistep interfacial reaction mechanisms is illustrated with some recent results obtained in our laboratory, utilizing potential-sweep voltammetry with simultaneous time-resolved SERS and IRRAS spectral acquisition. The presentation here is limited to a brief overview of representative findings; experimental and other details are given in the references cited.

Surface Raman and Infrared Spectral-Electrochemical Comparisons

As already noted, a commonly perceived difficulty in employing SERS for molecular surface characterization is that the technique may sample chemically atypical adsorbate molecules as a result of selective enhancement at the anticipated minority of "SERS-active" surface sites. One means of checking this possibility is to compare potential-dependent SERS spectral features for redox-active adsorbates with corresponding surface concentration-potential data obtained from electrochemical perturbation methods. Although the available data are scarce, good agreement between the spectral and electrochemical data is seen for several reversible redox couples involving adsorbed transition-metal complexes^{3,4d,7} indicating compatibility of the redox thermodynamics. Comparisons may also be made between the redox reactivity of the SERS-active and preponderant adsorbates that undergo irreversible electroreduction or oxidation by examining potential-dependent SERS intensities in relation to corresponding steady state or linear-sweep voltammetric current-potential data. Some deviations between the SERS and electrochemical reactivity data have indeed been observed. Thus the steady-state electroreduction of SERS-active adsorbed $\text{Cr}(\text{NH}_3)_5\text{NCS}^{2+}$ and $\text{Cr}(\text{NH}_3)_5\text{Br}^{2+}$ at a rotating silver electrode occurs at lower overpotentials (i.e. is more facile) than inferred from electrochemical data,⁸ whereas the opposite is observed for the electrooxidation of adsorbed carbon monoxide at platinum and palladium-coated gold.^{5c} Nevertheless, counter-examples are known (vide infra),^{4d,4h,8} and such deviations are unsurprising given the polycrystalline nature of the SERS-active surfaces.

More detailed insight into this matter can be obtained by comparisons between corresponding SERS and IRRAS spectra obtained under identical conditions. We have recently obtained such data for several anions and molecules adsorbed on gold and/or silver electrodes,⁹ as well as for CO on gold

coated with electrodeposited Pt and Pd overlayers.^{5c} For most of these systems, there is good agreement between the potential-dependent frequencies, ν , measured by SERS and IRRAS. An interesting exception, however, is CO on unmodified gold, for which the ν_{CO} frequencies differ by as much as 100 cm^{-1} , indicating that distinct species are being sensed by these two techniques.⁹ Significantly, electrochemical surface roughening of the polycrystalline metal surfaces, so as to yield SERS activity, yielded only minor increases in the infrared intensities with little change in the frequencies and bandshapes.⁹

Strategies for Coupling SERS and IRRAS with Reactive Electrochemical Techniques

As noted above, since absolute SER spectra can readily be obtained in conventional electrochemical cells, in principle this technique can be coupled with any electrochemical method compatible with the mutual temporal constraints. The simplest approach involves obtaining potential-dependent SER spectra for pseudo steady-state conditions using a rotating-disk electrode^{4b,8} along with the corresponding current-potential curves. Although such SERS data for irreversible redox reactions (i.e. where the faradaic current is controlled in part by heterogeneous kinetics) can shed light on adsorbate reactivity, the steady-state electrochemical data yields information only on the kinetics of the overall forward reaction.

The use of perturbation techniques, such as potential-step or sweep methods, are preferable since the electrochemical data so obtained can contain information on the kinetics of intermediate steps, especially involving adsorbed species. Using conventional instrumentation, these methods usually span timescales down to ca. 10^{-6} s . While it is certainly possible to acquire Raman spectra within such timescales, at least for irreversible electrode processes it is desirable to obtain a sequence of spectra during a single potential scan or following a single potential step since it is difficult to rapidly replicate such transients. When using conventional OMA instrumentation, to obtain each "single-shot" spectrum requires at least ca. 10^{-2} s . Given signal-to-noise constraints with our particular spectrometer/detector system (SPEX 1877/PAR OM-11) and using red (647 nm) laser excitation as is required for gold SERS, we typically require around 1-5 s to acquire each spectrum. While this necessarily restricts the timescale over which such coupled SERS-electrochemical measurements are made, mechanistically useful information can still be obtained. An example of coupled SERS-cyclic voltammetric measurements is given below.

In contrast to surface Raman spectroscopy, following the seminal work of Bewick and Pens electrochemical IRRAS has already been utilized by several research groups for examining reactive as well as stable interfacial species.² As noted above, IRRAS is commonly coupled to potential-step rather than optical

polarization modulation to obtain the required subtraction of solution-phase spectral interferences using both dispersive and Fourier transform spectrometers.² The acronyms "EMIRS" (electrochemically modulated infrared spectroscopy) and "SNIFTIRS" (subtractively normalized Fourier transform infrared spectroscopy) have been coined to denote these related potential-difference approaches² (referred to here in a more general vein as "PDIRS"). For chemically reversible electrochemical reactions (i.e. those for which the direction of redox processes can repeatedly be altered from products back to reactants upon appropriate potential reversal), an element of time resolution can be achieved by coupling the potential perturbation sequence with the spectral acquisition. With Fourier transform instrumentation, spectra may be obtained for timescales below that for a single interferometer scan by appropriately synchronizing the scans to the potential-step sequence.¹⁰

However, such potential-modulation approaches are inapplicable to the study of chemically irreversible processes since the limited quantity of reactant in the thin-layer reservoir cannot be regenerated by reversing the potential excursion. Potential-difference techniques employing dispersive infrared spectrometers are therefore inapplicable to the examination of such irreversible electrochemical processes, since a large number of potential modulations are required for referencing purposes during the slow wavelength scan. On the other hand, Fourier transform instruments can in principle be employed for this purpose since only a single potential-step or -sweep perturbation is required; desired co-added sets of interferometer scans obtained during the potential excursion can be referenced to that obtained prior to (or following) the perturbation.^{11,12} Admittedly, the timescale over which this "single potential-alteration infrared" (SPAIR) procedure can be applied will be limited by the time required to acquire sufficient S/N for each set of spectral scans; moreover, if the perturbation timescale is sufficiently long (say ≥ 1 min) difficulties can be faced in achieving spectral subtraction due to instrument drift. For this reason multiple potential modulations are normally employed even when PDIR spectra are obtained using FTIR instrumentation. Nevertheless, in suitable cases the SPAIR procedure can enable information to be obtained on the identity and reactivity of adsorbed species involved in multistep electrode processes, as exemplified below.

Examples of Coupled Surface Vibrational-Linear Sweep Voltammetric Characterization of Adsorbate Mechanisms

1. Electrooxidation of Adsorbed Benzidine. The elucidation of reduction or oxidation pathways of aromatic molecules forms an important segment of mechanistic organic electrochemistry;¹³ particularly in aqueous or other protic media complex multistep pathways are often encountered (or anticipated)

that involve adsorbed intermediates. We have recently been examining several such processes on gold electrodes by using SERS, including the reduction of nitrobenzene, azobenzene and related species, and the oxidation of benzidine and aniline.^{4h} Several of these systems are amenable to study using time-resolved SERS coupled with linear sweep voltammetry (LSV), especially since the reactants are typically irreversibly adsorbed, enabling the electrochemical reaction of the adsorbates to be examined without interference from solution-phase reactant.

Typical such data, for the electrooxidation of adsorbed benzidine, are shown in Fig. 1. The aqueous electrolyte, 0.1 M sodium acetate/0.1 M acetic acid, was chosen since it provides a buffered pH, 4.35, where the oxidation of solution-phase benzidine exhibits two reversible one-electron voltammetric waves at about 380 and 480 mV vs. the saturated calomel electrode (SCE).

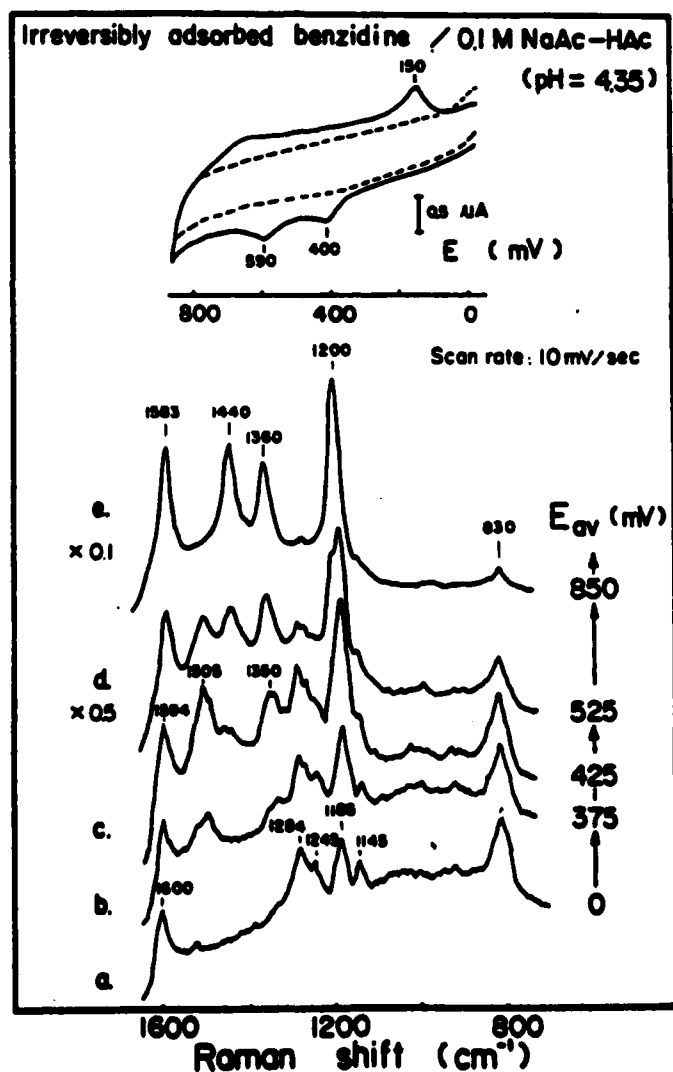


Fig. 1. SERS spectra (a-e) acquired (see text) during linear sweep voltammetric oxidation of adsorbed benzidine, at potentials indicated (vs. SCE). The anodic-cathodic cyclic voltammogram, shown above, was obtained simultaneously.

organic molecules, such as formic acid, methanol and ethylene glycol, that undergo irreversible electrocatalytic oxidation to CO_2 on platinum and other transition-metal surfaces, yield substantial quantities of adsorbed carbon monoxide in potential regions prior to where oxidation occurs.¹⁶⁻¹⁸ A significant remaining question, however, involves the possible role(s) of the adsorbed CO in the electrooxidation mechanism as an intermediate or poison.

Some information on this issue for formic acid and methanol oxidation at platinum has recently been obtained by examining the potential-dependent intensity of the C-O stretching mode, $\nu_{\text{C-O}}$, at progressively more positive potentials into the electrooxidation region by employing polarization-modulation IRRAS (PM-IRRAS).^{17b} (The virtue of the PM-IRRAS technique is that absolute infrared spectra can be obtained at a given potential, enabling the time and/or potential evolution of spectra resulting from irreversible electrode processes to be monitored.) The synergy observed between the electrooxidative removal of adsorbed CO and the onset of formic acid or methanol oxidation was suggested to signal the role of the CO as a poison for the latter processes.^{17b}

We have obtained similar data for these systems, but on a shorter timescale, by employing the SPAIR procedure (noted above) in conjunction with

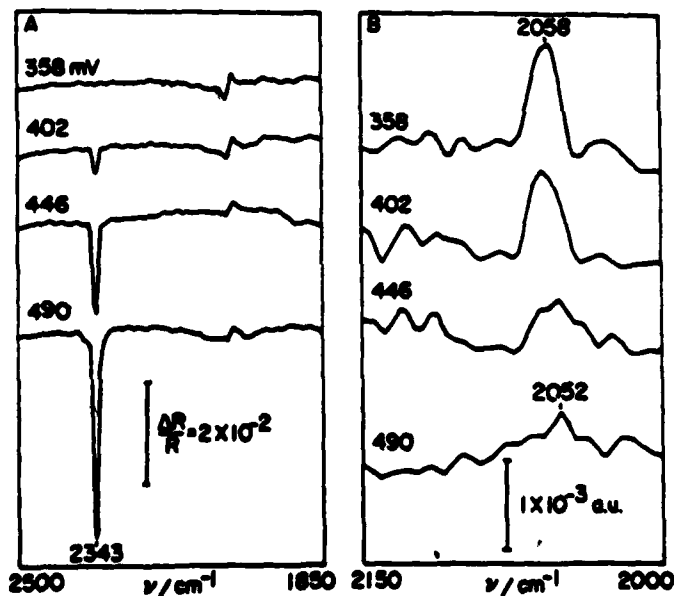


Fig. 2. SPAIR spectra obtained during a positive-going potential sweep at 2 mV s^{-1} from -0.2 V vs. SCE in 0.025 M CH_3OH + 0.1 M HClO_4 , after adsorption at -0.2 V for 20 min. (A) are relative reflectance spectra, obtained by acquiring a sequence of single-beam spectra (each using 5 interferometer scans) at the potentials indicated (mV vs. SCE), and ratioing these to the spectrum obtained at the initial potential. (B) are some corresponding absorbance spectra in the ν_{CO} region, generated by subtracting a spectrum obtained following CO electrooxidation (see text).

linear sweep voltammetry.¹² A few representative spectra, obtained during the electrooxidation of methanol on platinum ($25 \text{ mM CH}_3\text{OH} + 0.1 \text{ M HClO}_4$) are shown in Fig. 2A and B. These were obtained using a Bruker-IBM IR 98-4A FT instrument with an InSb detector; experimental details are given in ref. 12. The potential was swept in the positive direction from -250 mV vs. SCE at 2 mV s^{-1} ; each spectrum was obtained using 5 interferometer scans (consuming about 3 s). The spectra in Fig. 2A are referenced to that obtained at the initial potential just prior to the potential sweep; the average potential at which each spectrum was acquired is noted on the figure. The two features seen, the bipolar band around $2060\text{--}2070 \text{ cm}^{-1}$ and the intense negative-going feature at 2343 cm^{-1} are due to linearly adsorbed CO and bulk-phase CO_2 , respectively. The intensity of the latter band provides a quantitative measure of the extent of overall reaction occurring up to that point. In order to ascertain the potential dependence of the former feature, it is preferable to reference the SPAIR spectra to that obtained at a suitable positive value where the adsorbed CO is entirely oxidized, so to yield "absolute" ν_{CO} spectra. Such a spectral set, derived from those in Fig. 2A, is shown in Fig. 2B. (For convenience, the latter are plotted as absorbance spectra.)

Comparison between the corresponding potential-dependent CO_2 and CO band intensities in Figs. 2A and B shows that the potential region where the oxidative removal of adsorbed CO occurs corresponds closely to the onset of

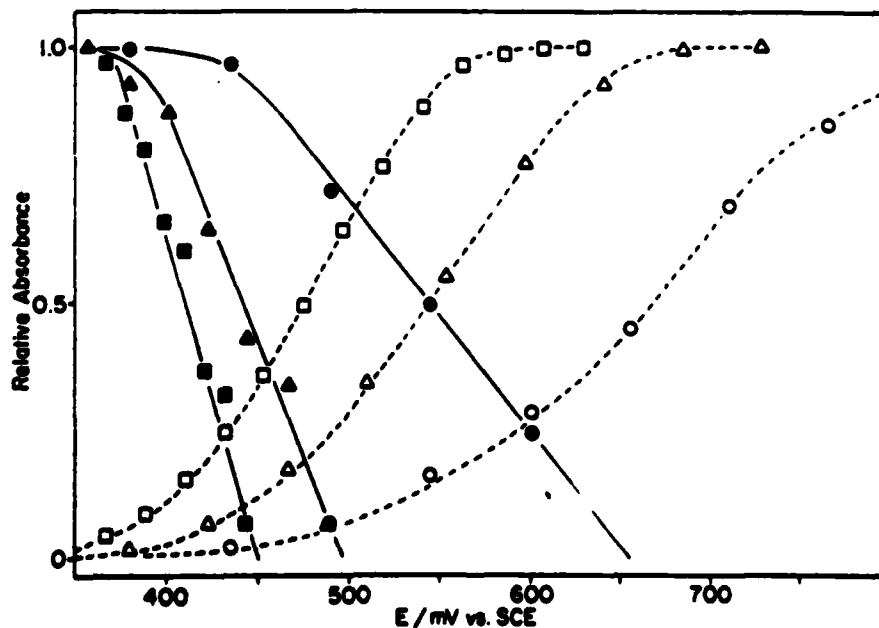


Fig. 3. Relative integrated absorbance of the ν_{CO} (filled symbols) and CO_2 stretching bands (open symbols) against electrode potential during linear potential sweep oxidation of methanol obtained from SPAIR spectra as in Fig. 2. Squares, triangles, and circles correspond to sweep rates of 1, 2, and 5 mV s^{-1} . Solution was $0.025 \text{ M CH}_3\text{OH}$ in 0.1 M HClO_4 .

methanol oxidation. This synergy is shown more quantitatively in Fig. 3 as plots of the relative absorbance of the ν_{CO} band (filled symbols) and of the CO_2 band (open symbols) against the electrode potential during such voltammetric sweeps. The squares, triangles, and circles correspond to sweep rates of 1, 2, and 5 mV s^{-1} , respectively. It is clear that a similar relation between the decrease in ν_{CO} intensity (and, approximately, therefore the CO coverage^{12,17b}) and the overall reaction kinetics is obtained in each case, even though the potential region where these changes occur depends on the voltammetric sweep rate.

Although these data are not inconsistent with the notion that the adsorbed CO is acting as a "poison" for methanol oxidation, it is also possible that the former is actually an adsorbed intermediate in the reaction pathway. In order to check this possibility, the adsorption kinetics of adsorbed CO from methanol were obtained from the time evolution of SPAIR spectra following suitable potential steps to values where the adsorbed CO is relatively stable to electrooxidation. The results, described in ref. 12, indicate that the CO readsorption rate is sufficiently rapid to account for the overall rates of methanol oxidation, at least under the conditions encountered here. A different conclusion was reached, however, for the role of adsorbed CO in formic acid oxidation on platinum.¹²

CONCLUDING REMARKS

Although applications of vibrational spectroscopy to the characterization of electrochemical adsorbates, especially reactive systems, are still in their infancy it seems clear that there are considerable opportunities for the utilization of both Raman and infrared spectroscopies in this regard. The outlook for electrochemical SERS given in the last Conference Summary in this series (VAS 4)¹⁹ appears to be unduly pessimistic, although perhaps understandable in view of some published literature in this area. While some controversies surrounding the physical origins of the SERS effect itself are yet to be settled, there are persuasive reasons to progress with further electrochemical applications of this method. The sensitivity of SERS, coupled with relative freedom from bulk phase interferences, wide frequency range and excellent frequency resolution make this technique well suited to the identification as well as characterization of reactive electrochemical adsorbates.

Given the constraints of SERS with regard to substrate morphology and composition, this technique can be viewed as being useful primarily in "applied" surface science. Especially given the widespread (and increasing) use of IRRAS in surface-gas phase systems, comparisons between the vibrational properties of these and related electrochemical systems are likely to employ

primarily infrared methods. The recently demonstrated techniques of surface-unenhanced Raman spectroscopy²⁰ may also contribute significantly in this regard.

Most importantly, methods for the in-situ vibrational characterization of electrode-solution interfaces are contributing increasingly to issues of real electrochemical significance involving reactive as well as stable adsorbates. Even though their impact upon electrochemistry so far has probably been smaller than in other branches of surface chemistry, their use is liable to expand in the near future. In particular, the use of vibrational techniques in combination with conventional electrochemical methods offers prospects for obtaining a detailed molecular view of electrode-solution interfaces that should foster greater overlap and comparison with analogous surface-gas phase systems.

ACKNOWLEDGMENTS

This work is supported by the National Science Foundation and the Office of Naval Research.

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structure 3. Comparable potential-dependent SER spectra were also obtained using solutions containing benzidine; negligible interference was experienced from the bulk-phase resonance Raman scattering from the dication, even though these spectra are themselves intense.

2. Role of Adsorbed CO in Methanol Electrooxidation on Platinum. A major application of electrochemical IRRAS so far is the demonstration that several

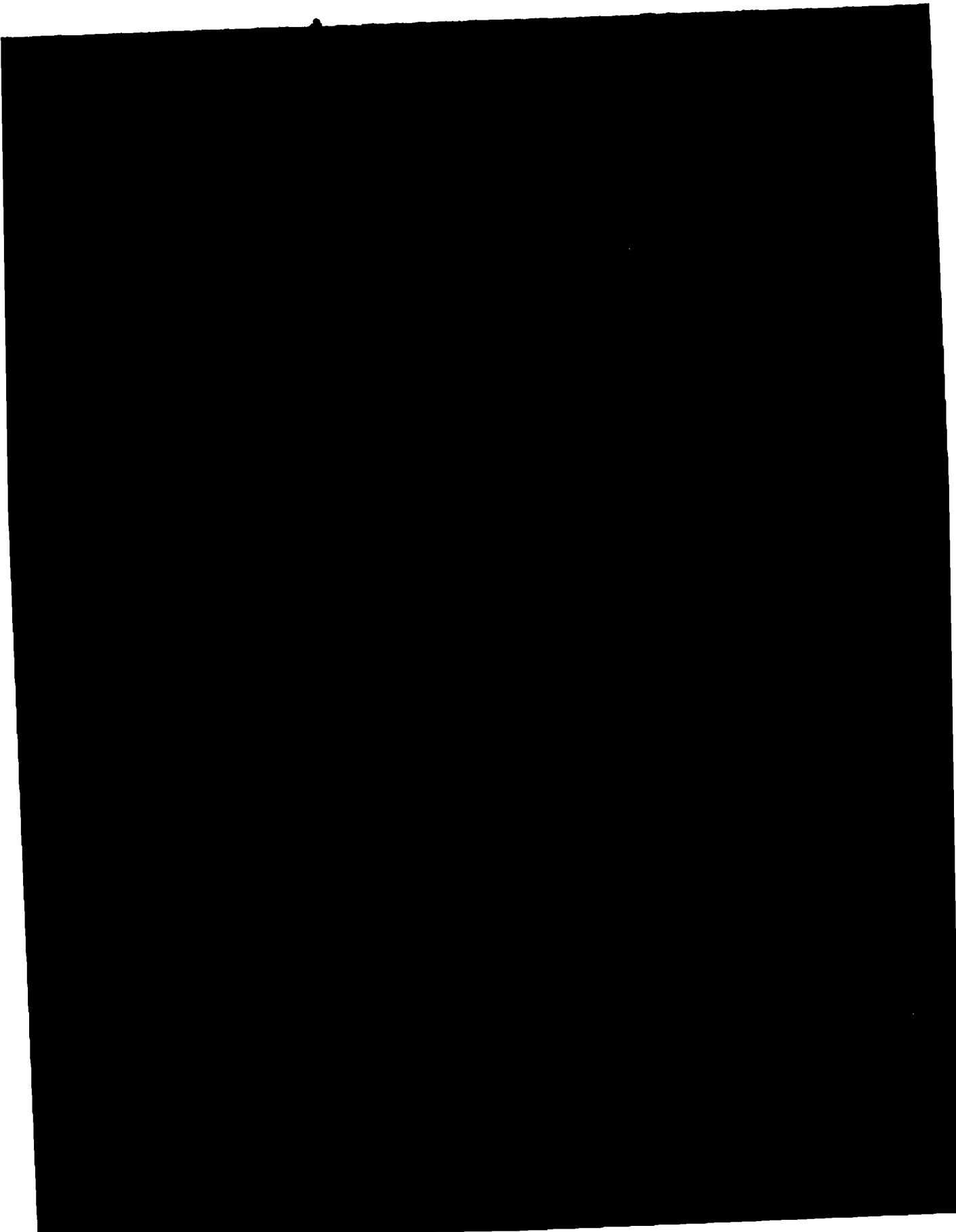
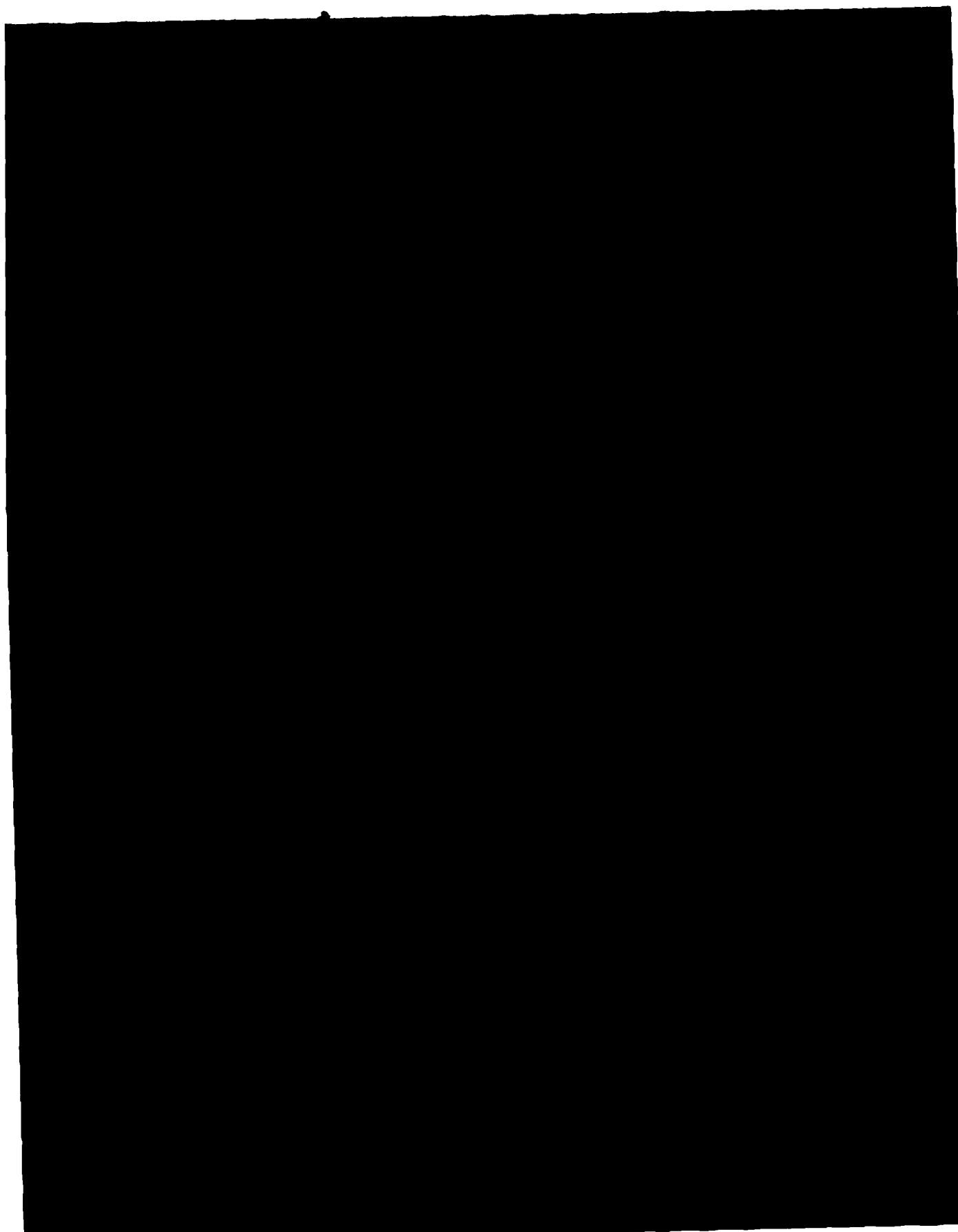


Fig. 2. SPAIR spectra obtained during a positive-going potential sweep at 2 mV s^{-1} from -0.2 V vs. SCE in $0.025 \text{ M CH}_3\text{OH} + 0.1 \text{ M HClO}_4$, after adsorption at -0.2 V for 20 min. (A) are relative reflectance spectra, obtained by acquiring a sequence of single-beam spectra (each using 5 interferometer scans) at the potentials indicated (mV vs. SCE), and ratioing these to the spectrum obtained at the initial potential. (B) are some corresponding absorbance spectra in the ν_{CO} region, generated by subtracting a spectrum obtained following CO electrooxidation (see text).



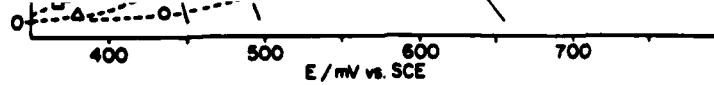


Fig. 3. Relative integrated absorbance of the ν_{CO} (filled symbols) and CO_2 stretching bands (open symbols) against electrode potential during linear potential sweep oxidation of methanol obtained from SPAIR spectra as in Fig. 2. Squares, triangles, and circles correspond to sweep rates of 1, 2, and 5 mV s^{-1} . Solution was 0.025 M CH_3OH in 0.1 M HClO_4 .

identification as well as characterization of reactive electrochemical adsorbates.

Given the constraints of SERS with regard to substrate morphology and composition, this technique can be viewed as being useful primarily in "applied" surface science. Especially given the widespread (and increasing) use of IRRAS in surface-gas phase systems, comparisons between the vibrational properties of these and related electrochemical systems are likely to employ

